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TECHNICAL NOTE

Patterning of platinum (Pt) thin films by chemical wet etching in Aqua Regia

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Abstract
The chemical and physical properties of platinum (Pt) make it a useful material for microelectromechanical systems and microfluidic applications such as lab-on-a-chip devices. Platinum thin-films are frequently employed in applications where electrodes with high chemical stability, low electrical resistance or a high melting point are needed. Due to its chemical inertness it is however also one of the most difficult metals to pattern. The gold standard for patterning is chlorine RIE etching, a capital-intensive process not available in all labs. Here we present simple fabrication protocols for wet etching Pt thin-films in hot Aqua Regia based on sputtered Ti/Pt/Cr and Cr/Pt/Cr metal multilayers. Chromium (Cr) or titanium (Ti) is used as an adhesion layer for the Pt. Cr is used as a hard masking layer during the Pt etch as it can be easily and accurately patterned with photoresist and withstands the Aqua Regia. The Cr pattern is transferred into the Pt and the Cr mask later removed. Only standard chemicals and cleanroom equipment/tools are required. Prior to the Aqua Regia etch any surface passivation on the Pt is needs to be removed. This is usually achieved by a quick dip in dilute hydrofluoric acid (HF). HF is usually also used for wet-etching the Ti adhesion layer. We avoid the use of HF for both steps by replacing the HF-dip with an argon (Ar) plasma treatment and etching the Ti layer with a hydrogen peroxide (H_2O_2) based etchant.

1. Introduction

Platinum has a number of material properties that can be exploited in microdevices. The range of applications is diverse and there are many in which other materials simply cannot be used. It is biocompatible, inert and has a high electrical conductivity, making it an excellent choice for electrodes. Pt has a high melting point (2045 K) and its electrical resistance changes linearly over a wide temperature range, enabling its use in resistive heaters, thermocouples and resistive temperature detectors. Due to its relative mechanical hardness, it is also used as a structural material in metal flexures and switch contacts [1].

These sought-after properties also make Pt inherently difficult to pattern. The method of choice for patterning fine Pt structures is dry etching with halide–argon based [2–9] or alternatively fluorine–argon based gas mixtures [10–12]. Ion milling/sputter etching with just Ar can also be used but is not selective to other materials and finding a suitable masking material is difficult [13–15].

However, the equipment needed for reactive ion etching (RIE) of Pt is not readily available in many labs. For this reason, a number of other methods have been reported in the literature: these include additive techniques such as lift-off and shadow masking, and subtractive patterning by wet etching. The limiting factors compared to dry etching are the feature sizes and aspect ratios that can be obtained.

Shadow masks are useful for structures where no freestanding features or structures with large aspect ratios are needed [16, 17]. During deposition the shadow mask can warp due to differential thermal expansion in the plasma, leading to hazy feature definition. As a rule of thumb the minimum shadow mask features should be around double the shadow mask thickness in order to get even deposition during sputtering. Smaller features down to potentially submicron could be patterned, but due to the fragility of these masks it

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is not possible to have arrays of patterns in close proximity. Masks for finer feature sizes are expensive, clog quickly and cannot be cleaned easily, severely limiting their use for Pt patterning.

For lift-off the Pt usually has to be deposited by evaporation since sputtering results in conformal coatings making it difficult to achieve clean lift-off. For successful lift-off following evaporation, an overhang resist profile has to be created. Various methods exist to achieve a favourable lift-off profile/geometry [18, 19] the most successful being a two-layer resist approach [1]. Thermal/resistive evaporation of Pt is difficult due to its high melting point. To prevent the resist mask from cracking, cooling steps have to be introduced and only short deposition cycles, i.e. thin-layers are deposited. E-beam evaporation is more favourable, but since the adhesion of evaporated films is not as good as for sputtered films, evaporation/lift-off of Pt is not suitable for structures where abrasion resistance or mechanical strength is required. Lift-off in general is not an ideal process and introduces the risk of particle formation.

Although wet etching in general is a familiar process in MEMS and microfluidic labs [20], the inert nature of Pt limits the choices of etchants and masking materials. The only practical wet etchant for Pt is Aqua Regia, a mixture of hydrochloric acid and nitric acid named for its ability to dissolve the noble metals [21–23]. Resist, polyimide and epoxy (SU-8) have been used as masking layers, but problems arise with mask attack and lifting. These masking layers cannot withstand longer times in hot Aqua Regia and can only be used for etching very thin Pt layers. The resulting Pt pattern is reported to display non-uniformity and poorly defined edges. A process combining lift-off and wet etching has been described [1, 24].

A method that does not require Aqua Regia has been reported by Zaborowski *et al*: a patterned layer of Ti on Pt with a Ti adhesion layer was covered with chemical vapour deposited glass and annealed at 600 °C to form a Ti/Pt alloy in the areas with a Ti/Pt/Ti sandwich structure. Following removal of the glass with hydrofluoric acid (HF), the alloyed areas were then etched with Piranha solution [25].

We present a simpler protocol for patterning Pt thin-films based on the use of a Cr hard mask layer showing excellent feature resolution. The Cr mask is patterned using conventional photolithographic techniques, and then serves as a mask for the Pt etch, as Cr is not readily dissolved by Aqua Regia. The adhesion layer (either Cr or Ti) is then removed, electrically isolating the Pt electrodes. A final Cr etching step then removes the mask layer. The process is fast, reproducible, and does not require any specialized equipment.

2. Fabrication

Multilayers with either Ti or Cr as permanent adhesion layer, a functional Pt layer, and Cr as a temporary masking layer were sputtered onto various 4″ wafer substrates such as borofloat glass (PlanOptik, Germany), Si with native oxide and Si with 200 nm SiO_2 (SiMat, Germany).

2.1. *Sample preparation*

The glass wafers were cleaned in a Piranha bath prior to loading, the silicon wafers were taken straight from the sealed wafer box. All wafers were sputter cleaned immediately prior to deposition in the chamber of a Nordiko RFG 2500 parallel-plate RF sputter coater for 5 min, 200 W, in argon (Ar) plasma at a pressure of 4×10^{-3} mBar.

2.2. *Sputter deposition*

Immediately following sputter cleaning Cr/Pt/Cr multilayers were deposited in the same Nordiko RFG 2500 parallel-plate RF sputter coater without breaking the vacuum (see figure 1(*a*)). A 72 nm Cr adhesion layer, followed by a 410 nm Pt layer and a 72 nm thick Cr masking layer was deposited.

Ti/Pt/Cr layers were deposited in two separate runs since the machine only supported two different target materials. First a layer of 30 nm Ti followed by 410 nm Pt was deposited. In a second run a 72 nm layer of Cr was deposited after changing the targets, pumping down to base vacuum again, and running a short sample sputter clean on the previously deposited Pt layer. One wafer at a time was loaded to improve thickness uniformity. The resulting metal sandwich layer exhibited excellent adhesion to the substrate as verified through an adhesive tape and scratch test.

2.3. *Cr patterning*

4″ wafers were cleaned in an O_2/Ar plasma in an Oxford Instruments Plasmalab 80 RIE and primed with hexamethyldisilizane (HMDS, Chestech, UK). An 800 nm thick layer of Shipley S-1813 (Chestech, UK) resist was spun onto the wafer (see figure 1(*b*)) and softbaked. The wafer was exposed in a maskaligner to a chrome mask and then developed in undiluted Microposit MF-319 (Chestech, UK). Resist residue in the developed areas was removed in the PlasmaLab RIE with a short O_2 plasma descum step before hardbaking the resist (see figure 1(*c*)). The Cr top layer was wet etched by immersing the dry wafer in freshly prepared CR-14 equivalent etchant (22% ceric ammonium nitrate, 9% acetic acid and 69% DI water, by weight [26]) (see figure 1(*d*)). The Cr underetch was checked with an optical microscope and the wafer soaked overnight in acetone to strip the resist mask. Any remaining resist was cleaned off in an O_2 plasma. It is essential to remove the Pt surface passivation caused by the O_2 plasma resist strip. This was achieved by exposing the wafer/Pt surface to a pure Ar-plasma immediately prior to starting the Pt etch (see figure 1(*e*)).

2.4. *Pt patterning*

For reproducible results the Aqua Regia (3:1 mixture of HCl and HNO_3) should be prepared shortly before use. The mixture was kept on a hotplate at around 60 °C throughout the etching process. Shortly after mixing, Aqua Regia begins to effervesce and develops a dark orange colour. When idle a lid was used to prevent evaporation from the beaker. For etching, the wafer was removed from the Ar plasma and immediately immersed into

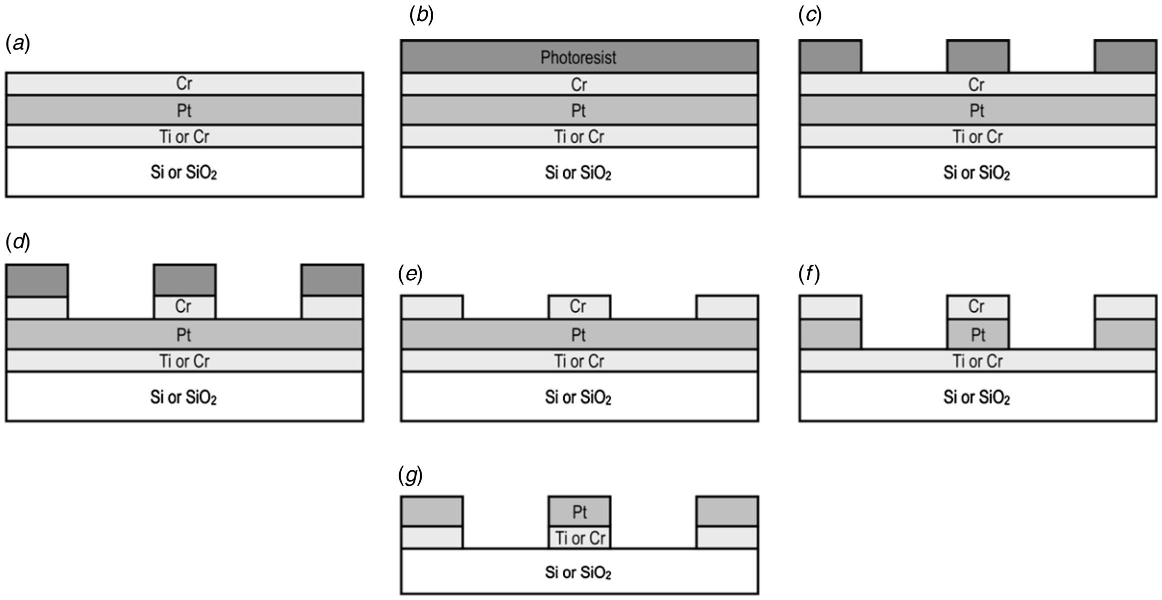

Figure 1. Process flow for the wet etching of platinum features using a chromium hard mask: (*a*) multilayer metal deposition; (*b*)–(*d*) photolithographic patterning of chrome hard mask; (*e*) removal of photoresist and platinum surface activation; (*f*) Pt etch in Aqua Regia; (*g*) removal of exposed adhesion layer and Cr hardmask.

the mixture. The exposed Pt layer was etched for 185 s, with no agitation (see figure 1(*f*)). Initially the exposed Pt layer will have a warmer golden colour compared to the colder silver-metallic colour of the Cr mask layer. As the etch progresses the Pt turns matte, whereas the Cr layer retains its mirror finish. In the samples where a Ti adhesion layer was used, the etch endpoint was visually obvious as the matte, light grey Pt disappeared in the etched areas and exposed the darker charcoal-grey Ti adhesion layer. In the samples where a Cr adhesion layer was used, the endpoint was reached when there was no longer any visual contrast between the layers. These differences can be observed through the Aqua Regia etching solution. It is important not to remove the sample too early for inspection as this will lead to passivation of the Pt and result in a severely reduced etch rate upon re-immersion in the etchant. After removal from the etchant the sample was washed with DI water and dried with compressed air.

2.5. Adhesion layer and Cr mask removal

The final step is the removal of the exposed Ti adhesion layer and the top Cr masking layer in order to expose and electrically isolate the Pt pattern. The Ti adhesion layer was removed by immersion in 1:2 solution of ammonia (NH_4OH) and hydrogen peroxide (H_2O_2, 30%) for 25 s. The Cr masking layer is removed using the previously described CR14 analogue etch. As no undercut is possible samples were left in the etchant for more than 2 min (see figure 1(*g*)). For Cr/Pt/Cr films the Cr adhesion layer was chosen to be the same thickness as the Cr mask layer, such that both can be etched away with a minimum of undercut in one step. The endpoint is visually obvious after ∼70 s.

3. Results and discussion

3.1. Cr versus Ti adhesion layer, adhesion layer thickness

Pt layers usually require a thin adhesion layer of e.g. Cr, Ti, Ta, Ti/W. For Cr/Pt/Cr films both Cr layers should be chosen to be of the same thickness to minimize any underetch of the Cr adhesion layer during the removal of the Cr masking layer. Choosing the same Cr thickness has the additional advantage of making it easier to detect when the top Cr masking layer has been removed. This is especially easy if the substrate is a glass wafer as the contrast between a thin Cr layer and a pure glass wafer is easily detectable. A Cr adhesion layer can also withstand a KOH etch, should this be required in a subsequent deep silicon etch. Replacing the Cr adhesion layer with a Ti adhesion layer has other advantages. Ti is a better choice for high temperature applications (up to 600 °C) [27]. Ti acts as a diffusion barrier and prevents interdiffusion to e.g. a silicon substrate and vice versa. The Ti adhesion layer is not attacked during the final removal of the top Cr masking layer and its thickness can therefore be chosen independent of the Cr thickness. In this case the Ti should be chosen with a typical adhesion layer thickness of around 30 nm. This again results in lower underetch of the Ti, which in turn allows the etching of finer Pt features. Figure 2 shows a typical etch result from a Ti/Pt/Cr sandwich structure, with clean, well defined structures. The EDX maps match the SEM and confirm that the Cr hard mask has been completely removed, revealing the Pt surface. The Pt structures have an excellent surface quality, with no pits or pinholes (see figure 3).

3.2. Cr and Pt surface passivation

Although Cr will dissolve in dilute HCl, it is suitable as a masking material for wet etching Pt in concentrated Aqua

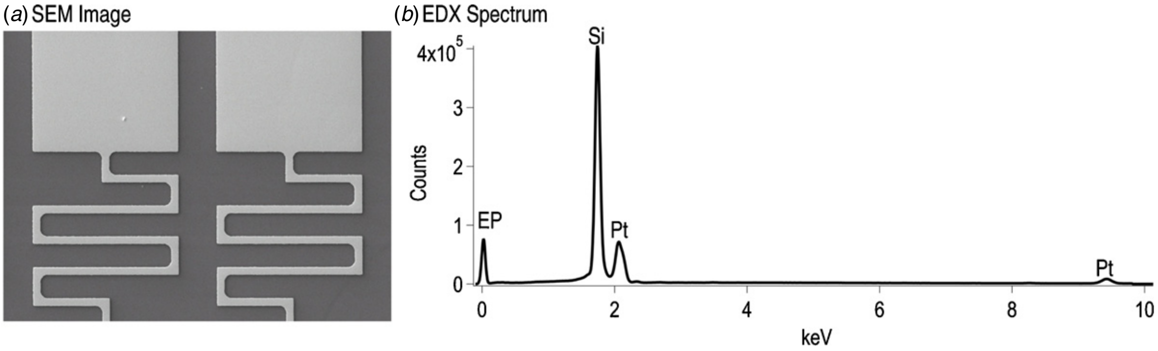

Figure 2. (*a*) SEM image and (*b*) corresponding EDX spectrum showing complete removal of the Cr mask from the Pt electrodes. The peak labelled EP is the detector escape peak.

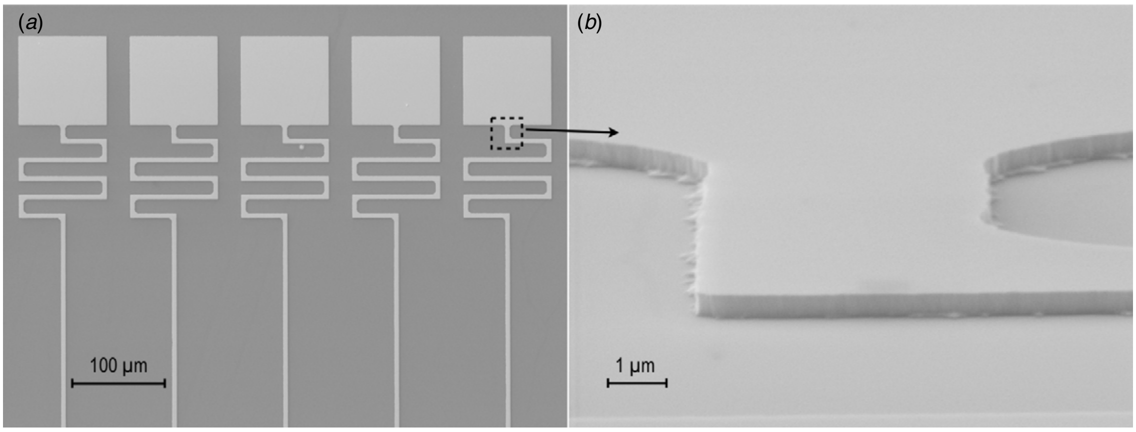

Figure 3. SEM images of wet etched Pt on a Ti adhesion layer.

Regia because Cr surfaces are passivated by strong mineral acids, whereas Pt is etched by the nascent chlorine produced during the process.

It was noticed, in line with the observations reported by Kim *et al* [28], that no matter how short an O_2 plasma clean was used on the samples it would lead to Pt surface passivation and that without a subsequent Ar-plasma step the sample could not be etched in the Aqua Regia, even if left in there for a relatively long time. If left for a very long time it would result in an etch reversal (observed after 80 min or longer) as the Cr masking layer would finally be removed and the underlying, non-passivated Pt would be etched. The onset of Cr etching in this case may be related to the decomposition of Aqua Regia, which leads to the evolution of chlorine, nitrosyl chloride and nitric oxide, effectively diluting the acids over time.

It is possible, as described by Kim *et al*, to pattern the Pt by passivating certain areas through a resist mask in an oxygen plasma, however it is difficult to remove resist residue to obtain a truly clean surface without the use of an O_2 plasma step, which in turn would passivate the entire sample.

3.3. Pinholes and etch artefacts

Cleaning/cleanliness of the substrate wafer before the multilayer sputter deposition was found to be very important. Any surface particles can easily lead to pinholes in the multilayer film, which are enlarged/exaggerated during the subsequent wet etching processes. The Cr mask layer needs to be chosen thick enough to protect the Pt layer for the duration of the etch. Any pinholes in the Cr are easily transferred into the Pt since it is not passivated underneath the masking layer. Especially in the Cr/Pt/Cr samples the pinholes are further exaggerated due to Cr underetch during the top Cr layer removal. It is best to hardbake the resist before the Cr etch to achieve minimum mask lifting during the etching and thus minimum underetch. The resist mask used for patterning the top Cr layer was removed before the Pt etch in Aqua Regia. It was found that when left on the wafer is usually was attacked by the hot Aqua Regia quite quickly and lifted off. Floating resist residue would randomly mask areas and leave an unpredictable, unclean etch result. It is therefore better to strip it off completely before the Pt etching step.

3.4. Feature size

The Ti/Pt/Cr sandwich approach yields good feature definition with sharp edges. The minimum feature size reliably etched across a 4″ wafer was 5 μm. However, we have not further investigated the achievable minimum feature size with the presented process.

The square pads on figure 3(*a*) had an edge length of 100 μm on the original masks. The Pt structures have an edge length of 98 μm, indicating a 1 μm underetch on either side. The inset, figure 3(*b*)) shows an enlarged area of figure 3(*a*) at an 80 degree tilt angle. The width of the meandering Pt trace is 5 μm, down from 10 μm on the original etch mask, indicating a 2.5 μm underetch on either side.

The smaller underetch of the larger structures compared to the smaller ones (see figure 3) may be due to depletion of etchant where more Pt is available for etching. This may also explain the differential etching seen on inside and outside edges of the meandering Pt trace, more easily seen in figure 2(*a*).

The smallest features successfully etched using Cr/Pt/Cr were significantly larger (approx. 25 μm). Undercuts of up to 8 μm (either side) in the 72 nm thick Cr adhesion layer were measured. As previously described, the Cr mask layer and Cr adhesion layer are removed at the same time. The Cr etch time is thus determined by the complete removal of the top Cr mask layer. This, in combination with a galvanic effect between Pt and Cr may explain the observed large Cr adhesion layer undercuts. No further optimization of the protocol was carried out.

The achieved feature sizes are useful for MEMS as well as lab-on-a-chip devices, especially for prototype work. Consistently etching smaller feature sizes will require much tighter process control and it is probably best, yield wise, to dry etch smaller features. For good wet etching results, especially of small features, the thickness distribution across the wafer should vary as little as possible. Best results were achieved when sputtering the Pt multilayers one wafer a time, centred on the substrate holder rather than multiple wafers in one sputter run.

4. Conclusions

A simplified method for Pt wet etching that does not require access to any equipment beyond that available in a basic MEMS lab is presented. The technique requires the deposition of only one additional Cr layer, which is patterned photolithographically and serves as a hard mask for the Aqua Regia Pt etch.

Both Cr/Pt/Cr and Ti/Pt/Cr multilayers were investigated. Various feature sizes were patterned, down to 10 μm lines (mask size), in 410 nm Pt using a 72 nm thick Cr hard mask. It should therefore also be possible to etch down to 10 μm features (mask size) in thinner Pt layers. Optimization of the various process parameters and various layer thicknesses may further improve the minimum feature size that can be achieved. The 72 nm thick Cr layer was able to withstand the Aqua Regia for around 80 min whereas the etch time for the 410 nm Pt layer was around 3 min. It is therefore likely that a Cr hard mask of this thickness may allow the patterning of thicker Pt layers, or vice versa, that a thinner Cr mask layer could successfully be used for patterning Pt layers up to ∼400 nm.

Appendix. RIE Recipes

The listed recipes are for the Oxford Instruments PlasmaLab 80 Reactive Ion Etcher.

Recipe/purpose	Parameters	Runtime (min)
Surface clean / resist strip	100 sccm O_2, 5 sccm Ar, 200 W, 100 mTorr, 20 °C	10
Resist descum	60 sccm O_2, 100 W, 50 mTorr, 20 °C	1
Pt surface activation	100 sccm Ar, 100 W, 50 mTorr, 20 °C	10

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